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COMPARATIVE DSC AND TG STUDIES OF THE DESORPTION OF WATER FROM CATIONIC-EXCHANGE RESINS

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ABSTRACT

A series of cationic-exchange resins have been studied by DSC and TG over the temperature range 25–200 ° C to determine the characteristics of water loss Both techniques provide comparable but complementary information The temperature at which the maximum rate of water loss occurs is found to be dependent on sample size, but generally lies within the range 80–90 ° C under standardized conditions The water capacity of the resins is shown to be strongly dependent on cation type ranging from as low as 13–17% for the potassium form to as high as 37–38% for H^+ or magnesium cations No significant variation is observed in heats of water desorption with respect to cation type, indicating that the bulk of the absorbed water may not necessarily be coordinated to the cation sites The resin water capacity is, however, shown to be related to the inverse of the cation size

INTRODUCTION

Cationic-exchange resins have been shown to exhibit useful properties as desiccants [1-5] and these materials have thus been applied to the problem of solvent drying An important variable in the application of cationic-exchange resins is the nature of the cation which is readily exchangeable The earliest studies [1] showed that the cation type had a significant effect on both the water capacity of the resin and the drying kinetics These results were confirmed in later studies [4,5] of water absorption from non-polar solvents where the inverse relationship between capacity and cation atomic weight was confirmed However, in the application of cationic-exchange resins for drying of polar solvents such as dioxane no significant difference was observed [3] in the drying efficiencies of a range of counter ions

An alternative approach to this problem is to study the desorption of bound water from the hydrated material since this will give a measure of the effective water capacity of the material Thermal techniques such as differential scanning calorimetry (DSC) and thermogravimetry (TG) are ideally suited for such studies since they permit the monitoring of water loss from the material by calorimetric or gravimetric means, respectively Parameters

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such as total water loss, heat of desorption and desorption temperature range should provide an insight as to the extent and strength of water binding

In this study a series of cationic-exchange resins have been prepared, allowed to equilibrate with atmospheric moisture, and the water loss subsequently studied as a function of temperature by both DSC and TG

EXPERIMENTAL

Materials

Sulphonic acid-type strong acid cation exchange resin (DOWEX MSC-1, sodium form) was provided as a gift by the Dow Chemical Co , U.S A The sodium form was acidified by treatment with 1 M hydrochloric acid and subsequently converted to other forms by treatment with appropriate nitrate solutions In each case the resins were washed with deionized water to remove excess electrolyte before air drying at 60 °C The resins were activated by heating at 140 °C in air overnight Subsequently, the activated beads were powdered and allowed to stand in equilibrium with the atmosphere for a period of 3 days so as to absorb atmospheric moisture

DSC analysis

All DSC measurements were made with a Perkin Elmer DSC-2C instrument equipped with a TA Data Station Powdered samples, ca 5 mg, were lightly crimped in standard aluminium sample pans and scanned over the temperature range from 17 to 227 °C at a scan rate of 10 °C min^{-1} The temperature scale was calibrated against standard samples of indium (156 65 °C) and zinc (419 52 °C) at a scan rate of 10 °C min^{-1} Peak temperatures and the enthalpy of desorption were calculated with the Perkin Elmer standard TADS programme

TG analysis

All TG measurements were carried out with a Mettler TA3000 thermogravimetric analyser over a temperature range of 25–250 °C at a scan rate of 10 °C min^{-1} Powdered samples, ca 10 mg, were contained in the supplied alumina crucibles equipped with lids and pin-hole exits, and were heated under an inert nitrogen atmosphere Weight loss steps were computed with the TC 10 data processor which forms an integral part of the Mettler instrument

Calibration of the temperature scale was accomplished by the Curie point method employing the standard materials supplied with the instrument

RESULTS AND DISCUSSION

DSC analysis

General features

The typical form of the DSC thermal curve for the dehydration of a cation exchange resin is illustrated in Fig 1 together with a base line obtained by rerunning the dehydrated resin It is significant that whereas the two thermal curves coincide at the high temperature end, there is a noticeable mismatch at the starting temperature This occurs because the heat capacities of the starting material and the dehydrated resin at 17 °C differ because of the presence of absorbed water in the former At high temperatures the water has been driven off and the two materials are identical and exhibit matching heat capacities At intermediate temperatures the difference between the two thermal curves is proportional to the heat capacity of the remaining bound water and the enthalpy of desorption of the water being driven off In these studies the value quoted as the enthalpy of desorption ΔH_{des} has been derived from the area under the observed curve bordered by the calculated line indicated in Fig 1 Almost certainly, the value so derived will include a contribution from the heat capacity of the bound water but this will not seriously invalidate the use of this quantity for comparative purposes

In addition to the value of ΔH_{des}, which is proportional to the amount of bound water, the thermal curves also provide the temperatures at which water loss begins (T_{ons}), occurs at a maximum rate (T_{max}) and is complete (T_{fin}) The general pattern is that water loss begins almost immediately, peaks at temperatures in the region of 80–90 °C and is complete at tempera-

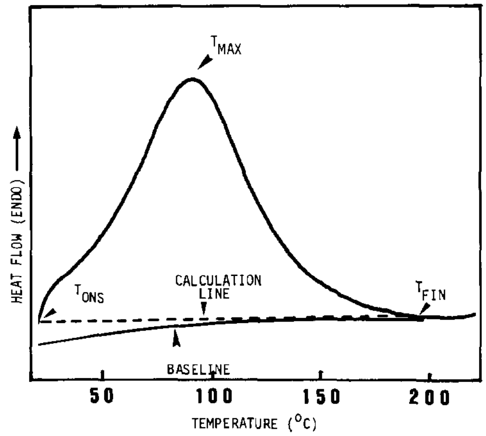

Fig 1 DSC thermal curve for water desorption from a DOWEX MSC-1 ion exchange resin, lithium form

tures approaching 200 °C By contrast, free water samples show an onset temperature close to 50 °C, a peak temperature close to the boiling point of water (100 °C) and a T_{fin} of about 110 °C The much broader thermal curves observed for all the ion-exchange resins implies that the water is present both as free water (contained in pores and channels) which is readily lost and as fixed water (coordinated to ionic sties and cations) which is only removed at higher temperatures The breadth of the temperature profile may also be partially a kinetic effect due to the slow diffusion of the moisture from the pores and cavities of the material

Effect of sample size and heating rate

In preliminary experiments it was judged prudent to examine the effects of heating rate and sample size on the observed water loss characteristics Study of a lithium ion-exchange resin showed that whereas the value of ΔH_{des} was approximately constant the value of T_{max} was significantly dependent on the scan temperature Thus, the observed T_{max} increased from a low of 64 °C at a scan rate of 2 °C min^{-1} to a high of about 110 °C at a scan rate of 25 °C min^{-1} Whereas this is partially due to instrument effects, the observed shift may be largely attributed to the kinetic features of the water loss process All subsequent DSC data reported in this paper were obtained at a fixed scan rate of 10 °C min^{-1} so as to provide standard conditions for comparison purposes

Sample size is also known to affect DSC data and so the acidified form of the exchange resin was examined using sample sizes in the range 1–10 mg The results for five sample sizes are summarized in Table 1 It is apparent that the T_{max} value progressively increases with sample size and this is presumably related to the diffusion control characteristics of the loss of water from increasing sample sizes Surprisingly, the value of ΔH_{des} is also substantially affected by sample size, particularly at very low sample sizes The reason for this is not completely clear, but it is possible that for very small samples significant errors may be introduced by water loss through the

TABLE 1

The influence of sample size on the observed water loss characteristics

Sample size (mg) [a]	T_{max} (°C)	ΔH_{des} (cal g^{-1}) [b]
1 09	69	103
2 46	84	155
3 44	83	152
5 23	88	163
5 44	91	161
10 21	106	152

[a] Weight refers to wet sample, i e resin + bound water

[b] ΔH_{des} expressed in calories per initial weight of whole sample Resin = Dowex MSC-1 acid form Scan rate = 10 °C min^{-1}

drying effect of the nitrogen gas stream prior to commencement of the heating run. Because of the significant effect of sample size all subsequent studies were carried out with samples in the range 5–5.5 mg.

One further point of interest is that free-acid type of the ion-exchange resin differs significantly in the form of the thermal curve from that of the metal cation resins. Thus, at high temperatures the acid form shows the onset of a second endotherm at about 170 °C and this is probably indicative of the onset of degradation reactions since the acid form is known [1] to be less thermally stable than the salt forms which may be regenerated at temperatures as high as 195 °C.

Effect of cation type on water absorption and loss

A series of eight distinct cation types as well as the free-acid form of the resin were examined in a comparative study, the results of which are summarized in Table 2. In these studies the weight loss of the sample was also recorded by measurement of the encapsulated sample mass immediately before and after DSC measurement and these values are also tabulated. It is immediately apparent that the resin capacity is dependent on the cation type with observed bound water ranging from as low as 13% for the potassium form to as high as 37% for the acid form. These results are generally in agreement with earlier studies [1] that showed a capacity exceeding 34% for

TABLE 2

Water loss characteristics of a series of ion exchange resins as monitored by DSC

Cation	Atomic weight	Ionic radius (Å)	Weight Loss [a] (%)	Resin capacity [b] (g H_2O (g dry resin)$^{-1}$)	T_{max} (°C)	ΔH_{des} [c] (cal g^{-1})	ΔH_{des} [d] (cal (g H_2O)$^{-1}$)
H^+	1		26.8	0.37	88	163	609
Al^{3+}	30	0.5	25.4	0.34	88	155	609
Li^{2+}	6.9	0.6	22.5	0.29	85	130	579
Mg^{2+}	24.3	0.65	26.1	0.35	86	150	576
Zn^{2+}	65.4	0.74	21.8	0.28	85	138	633
Na^{2+}	23	0.95	17.9	0.22	81	114	638
Ca^{2+}	40	0.99	18.7	0.23	82	117	626
Sr^{2+}	87.6	1.13	13.6	0.16	77	95	695
K^+	39.1	1.33	11.2	0.13	80	78	695
							Mean = 629

[a] Determined from weight of sample pan + sample after DSC run.

[b] Resin capacity expressed as weight of bound water per unit weight of dry resin.

[c] ΔH_{des} expressed in calories per initial weight of whole sample.

[d] ΔH_{des} expressed in calories per unit mass of water lost. Resin = Dowex MSC-1 with cations as indicated. Scan rate = 10 °C min^{-1}.

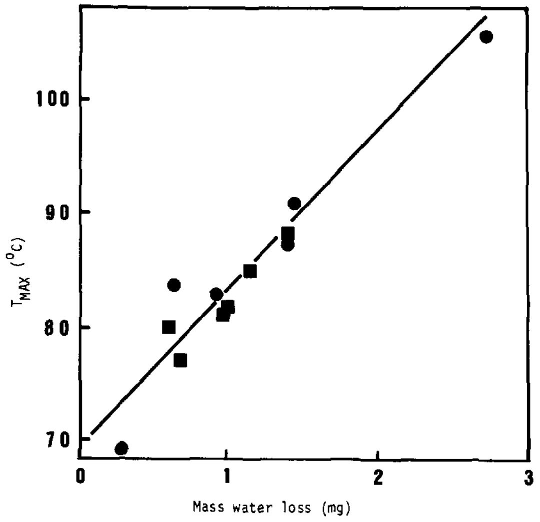

Fig 2 The relationship between the temperature of maximum rate of water loss (T_{max}) and the mass of desorbed water ●, Data from acid form but variable sample size, ■, data from various cation types and sample size of 5 mg

the acid form employed in drying of non-polar solvents An inspection of the physical characteristics of the cations shows that the bound water content is approximately related to the size of the ions, bound water increasing as ionic size decreases A second apparent trend is that the T_{max} value also varies with the nature of the cation and it would be tempting to conclude that the higher T_{max} values encountered with small ions reflects stronger binding of the water However, comparison of these results with those obtained on variation of sample size shows quite clearly that the T_{max} value is simply related to the amount of bound water released (Fig 2) and does not reflect any special characteristic of the cation

The measured value ΔH_{des} for the whole sample is seen to parallel the weight loss and is an effective measure of the bound water content of the resin even without separate gravimetric determination Calculation of ΔH_{des} per gram of water lost gives values in the range 576–695 cal g^{-1}, with a mean of 629 cal g^{-1} These values exceed the ΔH_{vap} value of water at its boiling point (540 cal g^{-1}), but this is not unreasonable since the value must also include the heat required to raise the temperature of the water Examination of the values shows that there is no clear correlation with any of the ionic parameters and therefore no evidence of characteristic differences in binding of the water. It is, of course, possible that a substantial part of the water absorbed by the resins is not actually coordinated to the cations but merely contained in the pores and channels In this case the predominant binding energy would be hydrogen bonding between neighbouring water molecules

TG analysis

The same samples were also analysed under similar conditions by thermogravimetry However, although the same heating rate was employed samples were contained in alumina crucibles fitted with pin-hole lids and somewhat larger (10 mg) samples were used The water-loss data were analysed by the conventional weight-loss curve and the derivative curve (DTG) The form of the DTG curve is seen to be quite analogous to that of the DSC curve (Fig 3) with immediate weight loss at low temperatures, a peak in rate of weight loss at around 80 °C and a stable weight at about 200 °C

The data from the TG curves for a series of different cation types are summarized in Table 3 It can be seen that the TG data is quite similar to those obtained from the DSC study Thus, the value of T_{max} is generally quite close Presumably, the larger sample size is compensated by the different geometry of the sample crucibles compared to the crimped sample pans used for the DSC study

A more careful analysis of the relationship between resin capacity and cation type shows that there is an approximately inverse relationship between the bound water content and the radius of the cation (Fig 4) Of some interest is the observation that the slopes of the lines are different for the singly and doubly charged cations indicating that the charge/radius ratio is of some significance in determining binding of water Thus, for the same radius, doubly charged cations have greater capacity than singly charged ones It is also significant that Fig 4 displays a positive intercept implying

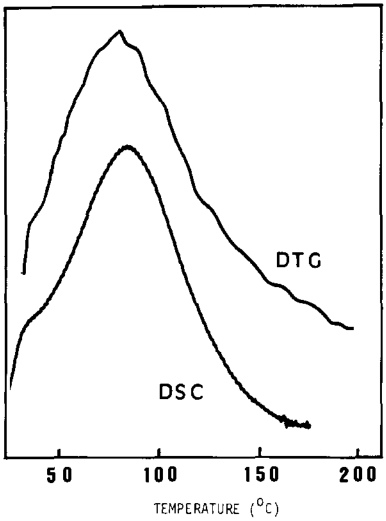

Fig 3 Comparison of the forms of the DSC and DTG thermal curves for the same sample of DOWEX MSC-1 ion exchange resin, potassium form

TABLE 3

Water loss characteristics of a series of ion-exchange resins as monitored by TG

Cation	Ionic radius (Å)	Weight loss (%)	Resin capacity (g H_2O (g dry resin)$^{-1}$)	T_{max} (°C)
Al^{3+}	0 5	27 5	0 38	88
Li^+	0 6	25 7	0 35	85
Mg^{2+}	0 65	27 3	0 38	87
Zn^{2+}	0 74	26 8	0 37	87
Na^+	0 95	19 3	0 24	77
Ca^{2+}	0 99	22 8	0 30	86
Sr^{2+}	1 13	19 4	0 24	79
Ba^{2+}	1 35	18 1	0 22	75
K^+	1 33	17 0	0 20	77

Resin = Dowex MSC-1 with cations as indicated Scan rate = 10 °C min^{-1} Sample size = 10 mg

that there are sites for water adsorption which are independent of the cation type This common intercept could perhaps be attributed to the sulphonate anion

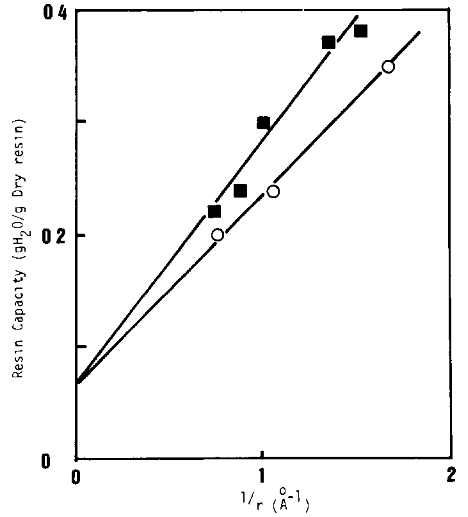

Fig 4 Correlation of the dry resin water capacity with the inverse of the cation radius ○, Mono-valent cations, ■, divalent cations

SUMMARY

The results of this study show that DSC and TG analysis of water desorption provides similar but complementary information The cation type is shown to exert a significant effect on the capacity of the resin to absorb water The failure to observe such effects in earlier studies [3] of drying of polar solvents must be attributed to competitive absorption of the polar solvents on cation sites which reduces the observed differences in capacity

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